ULTRA-LOW SULFUR DIESEL IMPLEMENTATION WORKSHOP

Summary of ASTM ULSD Crosscheck Program Results

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Program Objectives

1. **Provide an opportunity for labs to gain experience measuring diesel sulfur concentrations at 15 ppm or less.**
2. **Provide a comparison of measurement results from several test methods (i.e., ASTM D 2622, D 3120, D 5453, D 6920 and PBMS).**
3. **Participating labs are provided a confidential means to compare their performance against other labs worldwide.**

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Program Objectives

4. **Lab performance can be compared to US EPA and CARB enforcement labs to monitor any biases.**
5. **Program provides a source of QC reference samples.**

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Status Report

- Monthly Program Launched in January 2004
- Cost $1,080 per Lab
- A 150 ml Sample Supplied
- Level of Sulfur is 1–15 mg/kg
- Density Value Supplied
- Each Sample is to be Analyzed in Duplicate
- 105 Labs are Participating (14% Non-Continental US)

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Status Report - continued

- Four Methods are Used: D 2622; D 3120; D 5453; D 6920
- Typical Number of Labs Reporting Per Method

  D 2622 @ 49
  D 3120 @ 7
  D 5453 @ 58
  D 6920 @ 3

- Since April 2004, Labs Were Asked to Include a Check Standard in the Analysis

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Statistical Results

- Table of individual lab reported data
- Individual lab Z scores
- Data distribution graphs
- Robust mean (mean of retained data)
- Robust standard deviation (SD/0.882)
- Repeatability (r)
- Reproducibility (R) [2.77 times the robust standard deviation]

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2004 ASTM ULSD Crosscheck Program (mg/kg)
(Robust Mean ± Robust Standard Deviation)

Month	D2622	D3120	D5453
January	15.18 2.29 EPA: 16	13.35 3.46	15.08 1.47 CARB: 13.8

2004 ASTM ULSD Crosscheck Program (mg/kg)
(Robust Mean ± Robust Standard Deviation)

Month	D2622	D3120	D5453	D6920
January	15.18 ± 2.29 EPA: 16	13.35 ± 3.46	15.08 ± 1.47 CARB: 13.8	13.80, 15.35
February	2.35 ± 1.76 EPA: 5	1.53 ± 0.52	1.58 ± 0.47 CARB: 1.3	1.05, 1.76, 0.30
March	1.86 ± 1.52 EPA: NA	1.53 ± 0.40	1.41 ± 0.44 CARB: 0.9	1.50, 1.10, 0.95, 0.30
April	15.41 ± 2.13 EPA: NA	15.05 ± 0.91	14.92 ± 1.42 CARB: 14	15.55, 19.00, 12.55
May	10.48 ± 1.79 EPA: NA	9.89 ± 0.67	9.83 ± 0.98 CARB: 9.15	9.40, 9.70, 0.50
June	0.48 ± 0.57 EPA: NA	0.90 ± 0.63	0.66 ± 0.40 CARB: 0.3	-1.15, 1.20
July	4.01 ± 1.47 EPA: NA	3.57 ± 0.50	3.49 ± 0.59 CARB: 2.95	4.0

2004 ASTM ULSD Crosscheck Program
(Repeatability (r) and Reproducibility (R); mg/kg)

Month	Approx Sulfur Level	D2622*		D3120		D5453	
		r	R	r	R	r	R
January	15	2.12	6.38	0.37	9.98	0.46	4.09

2004 ASTM ULSD Crosscheck Program
(Repeatability (r) and Reproducibility (R); mg/kg)

Month	Approx Sulfur Level	D2622*		D3120		D5453		D6920**	
		r	R	r	R	r	R	r	R
January	15	2.12	6.38	0.37	9.98	0.46	4.09		
February	1.6	1.22	4.89	0.33	1.49	0.18	1.31		
March	1.5	0.49	4.22	0.00	1.10	0.19	1.22		
April	15	1.69	5.92	1.34	2.57	0.49	3.94		
May	10	1.43	4.96	0.35	1.88	0.37	2.72		
June	0.7	0.84	1.59	0.00	1.77	0.78	1.11		
July	3.6	1.21	6.01	0.00	1.77	0.17	1.64		

* Because the data do not represent a normal distribution fit, the precision results should not be interpreted in accordance with conventional normal distribution probabilities (i.e., Anderson Darling >1.3)

** Precision results are not provided because the required minimum number of labs did not report data using D6920

General Conclusions

- Most labs use D 2622 and D 5453
- Generally, robust means from D 2622, D 3120 and D 5453 are comparable, i.e., no apparent bias
- Reproducibility is a function of sulfur level, and test method

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Recommended ASTM Action on Outliers

1. Check results for typos, calculation errors and transcription errors
2. Reanalyze sample; check for repeatability
3. Check sample for homogeneity or contamination, and that a representative specimen has been analyzed
4. Review test method, and ensure that the latest version is being used; check procedure step by step with analyst

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Recommended ASTM Action on Outliers - continued

5. Check instrument calibration
6. Check QC chart to see if problem has been developing earlier
7. Check quality of reagents and standards; determine if they are expired or contaminated
8. Check equipment for proper operation against vendor's operating manual

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Recommended ASTM Action on Outliers - continued

9. Call vendor for maintenance and/or repairs
10. After resolution, analyze a CRM or lab QC sample to ensure that analysis is under control
11. Provide training to new analysts and, if necessary, refresher training to experienced analysts
12. Document incident and what was learned for use in resolving similar problems in the future

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